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SOURCE EMISSION MEASUREMENTS OF VOLATILE ORGANIC CHEMICALS

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16. ABSTRACT

Analytical methods for measuring volatile organic compounds were reviewed. Two commercially available instruments were selected and evaluated in the laboratory; one was judged unacceptable. The other analyzer was evaluated during a limited field test; results were satisfactory and averaged 3% higher than results produced by a concurrently operated gas chromatograph system.

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ABSTRACT

This report includes a literature survey of methods for the measurement of volatile organic compounds, and selection and evaluation of two commercially available analyzers. Instruments made by Baseline and Dohrmann were tested under laboratory conditions. The Dohrmann instrument was also compared against a gas chromatograph at a maleic anhydride plant. The Dohrmann analyzer averaged 3% higher than the gas chromatograph for 16, 1-hr integrated gas samples.

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SECTION 1

INTRODUCTION

The emission of volatile organic chemicals adversely affects air quality either directly by being a toxic material or indirectly by participating in photochemical reactions to form oxidants. Therefore, it is necessary to regulate volatile organic emissions to the atmosphere.

The Environmental Protection Agency (EPA) has undertaken a long-term program to regulate the synthetic organic chemical manufacturing industry (SOCMI), specifically the segment of the industry involving organic intermediates. The industry will be evaluated using gas chromatography (GC) and sampling techniques that are compatible with the process being investigated. The compliance test procedure is expected to be based on the measurement of volatile organic compounds (VOC). This technique has been selected to eliminate errors related to the varying response factors associated with the use of a flame ionization detector (FID). Since the VOC measurements approach is to be used by the Office of Air Quality Planning and Standards (OAQPS) for compliance tests, more information is required on VOC methods to determine if it is a viable test method.

The objective of this program is to select the best methods for measuring VOC which are applicable to field measurements of hydrocarbon emissions. The scope of this program is dividied into three tasks and a field test. Task I consists of a literature search encompassing the years 1967 through 1977 and an evaluation of the methods available. Task II consists of locating sources of analyzers employing the methods identified under Task I and obtaining the use of the best analyzers for evaluation. Task III consists of a laboratory evaluation of the analyzers and the development of a prototype field calibration unit. The field test consists of selecting a suitable source in the SOCMI, obtaining permission to conduct the tests, and conducting a field test of the analyzers evaluated.

SECTION 2

CONCLUSIONS

The laboratory tests indicate that the Dohrmann analyzer is capable of reliable measurements of a variety of organic sample streams with good rejection of CH_4, CO, and CO_2 while maintaining complete recovery of other organics including ethane and ethylene. The linearity at medium to high organic concentrations is good, but below a few hundred parts per million carbon, the background seriously affects linearity in the prototype system.

The reproducibility of the background readings results in a detection limit of 2 to 10 ppm as carbon at present, although continuous use and great care in maintaining supply gas purity should allow some improvement in the detection limit. Operating the analyzer with the gain at maximum and a 10-cc sample loop results in one count of the integrator being equivalent to 0.2 ppm carbon.

The overall precision and comparability for the GC and Dohrmann indicate that the Dohrmann can perform satisfactorily under field conditions at maleic anhydride processes. It should be noted that this test cannot demonstrate the accuracy of the results but rather the equivalence of the VOC method with the summation of all observed GC peaks. The equipment setup, stabilization, and operating environment requirements of the Dohrmann are not significantly different from those for a small GC which can make the instrument suitable for many field studies within the limits of the approximately 9-min analysis cycle time.

SECTION 3

LITERATURE REVIEW

The concentration of VOC in aqueous media and the concentration of total hydrocarbons (THC) in the atmosphere are generally accepted as reliable indicators of the amount of pollution present from organic chemicals from industries and natural sources. At specific concentrations, these organic contaminants present an acute or latent hazard for people, plants, and animals. Therefore, it is important to monitor the amount of organic contaminants present in the air and water. The kind of data desired from monitoring programs is information that will provide a reliable assessment of the degree of pollution in different environmental media (i.e., air and water).

Several methods have been developed for the determination of VOC and THC in water and the atmosphere. This is a review of work that has been done in this area, covering selected methods from 1967 to the present time which are representative of commercially available analytical methods suitable for monitoring organic pollutants from industrial and natural sources.

This literature survey was conducted using a computerized search of Chemical Abstracts from 1970 to the present and by a manual search of the technical literature prior to 1970. A total of 29 references were obtained which appeared to be directly applicable to the intent of this review. A bibliography lists 46 additional references which were reviewed as well.

The objective of this survey is to study methodologies suitable for source air sampling and analysis. However, a substantial amount of research and development has been conducted in the water area. Therefore, a discussion of the methods used in water analysis is included, as the discussion will aid in the understanding of organic chemical measurements.

GENERAL PRINCIPLES OF ANALYSIS

The first instrument to measure carbon levels in aqueous samples was developed by Dow Chemical Company and licensed to Beckman Instruments, Inc. The basic principle of that instrument is still used today. It consisted of a catalyst-packed combustion tube housed in a high temperature furnace and a nondispersive infrared (IR) detector sensitized to carbon dioxide. Any inorganic or organic carbon compounds were decomposed to CO_2, and the resulting analysis of the instrument was of total carbon. Methods of sample preparation were developed to eliminate inorganic carbon from the sample, and this made it possible to determine VOC.

One of the most significant developments in recent years has been VOC analyzers that do not require sample preparation to remove inorganic carbon. In addition to the high temperature combustion furnaces that were on the first carbon analyzers, these VOC analyzers have a separate second channel consisting of a low temperature furnace at 150°C which heats a tube containing quartz chips coated with phosphoric acid. Inorganic carbon compounds in samples injected in this tube are decomposed to carbon dioxide by acid and heat. Because of the low heat and the absence of a catalyst, organic compounds are not oxidized in passing through the column. In the analyzer, the high temperature furnace converts all carbon compounds to CO_2; the low temperature furnace converts only the inorganic carbon compounds to CO_2. Subtraction of the inorganic carbon contribution from the total carbon concentration yields the total organic concentration. More recently developed VOC analyzers convert CO_2 to methane and utilize an FID for final determination.

For air analysis, the THC analyzer is used to determine organic pollutants. Determinations are made by direct sample injection to an FID or by the combined use of GC and flame ionization.

Techniques to reduce interferences such as moisture, nitrogen, and other air constituents by using stripping techniques and molecular sieve separation columns have improved the performance of GC-FID methods. In addition, the use of fully automatic models has reduced the time required for analysis.

AIR ANALYSIS

The FID is generally accepted as being the preferred detection method for the total carbon content of a mixture of hydrocarbons. All commercially available THC analyzers are similar; they are based on the ionization produced when a hydrocarbon sample is injected into a small hydrogen diffusion flame.

When the FID is combined with a GC, the system has the capability of determining THC or individual compounds. By backflushing the GC column, THC can be determined; using the foreflush, individual components are eluted and determined.

The GC combined with a mass spectrometer (MS) was found to be the tool most often used for analyses of the complex air samples likely to be found in industrial situations. Two other methods appear in the literature: a portable IR spectrophotometer (Brady, 1975) and a portable MS which employs a silicone membrane material for hydrocarbon separation from air gases (Evans and Arnold, 1975).

Table 1 provides a list of methods representative of the state of the art of THC analyzers from air samples.

Flame Ionization Method of THC Analyzers

Several commercially available THC analyzers are designed to measure continuously the concentration of organics in the atmosphere.

TABLE 1. TOTAL HYDROCARBON ANALYSIS

Instrument	Principle of method	Detection method	Components measured	Lower detection limit	References
THC	Direct sample ionization	Direct FID	Total hydrocarbons	13 mg/m^3 or 20 ppm	Katz (1977)
THC	Backflush chromatography	GC/FID	Total hydrocarbons and individual compounds	1 mg/m^3	Eaton et al. (1973)
Hewlett-Packard Model 5830A THA	Backflush chromatography	GC/FID	Total hydrocarbons and individual compounds	0.1 ppm	Burgett and Green (1976)
GC/MS	Capillary column separation	GC/MS	Individual compounds		Pellizzari et al. (1976)
Perkin-Elmer Model 900 GC	Backflush chromatography	GC/FID	Total hydrocarbons and individual compounds	0.1 ppm carbon	Dimitriades and Seizinger (1971)
UTI Model 100B quadrupole analyzer	Silicon membrane separator	MS	Individual compounds	5 ppm	Evans and Arnold (1975)
Perkin-Elmer Model 900 GC	Capillary column separation	IR spectra	Individual compounds	5 ppb	Brady (1975)
Byron Instruments, Inc. Model 233 GC	Molecular sieve separation columns	GC/FID	Individual compounds	< 1 ppm	Byron Instruments
Baseline Industries, Inc. Series 1030 GC/FID	Backflush chromatography	GC/FID	Individual compounds and total hydrocarbons	Low ppb range	Forsberg (1978)

Measured volumes of air are delivered at preset intervals through a sample line attached to the inlet port of the FID. An electrometer coupled with a potentiometric recorder detects the increase in ion intensity resulting from the introduction of an air sample into the hydrogen flame. The response to the organic components is approximately proportional to the number of carbon atoms in the sample. The analyzer is calibrated using methane, and the results are reported as methane equivalents.

The detection limit for flame ionization is 0.001 ppm. The upper limit is much greater than the concentration normally encountered in the air. The different organic species present in the air sample (e.g., hydrocarbons, alcohols, ketones, etc.) can cause varying degrees of detector response. The FID does not distinguish between individual organic compounds or hydrocarbon classes without prior separation procedures (Katz, 1977).

A variation in the above method is used to determine nonmethane hydrocarbons. In this procedure, an aliquot of the sample air delivered to the FID is introduced into a stripper column which removes water, carbon dioxide, and hydrocarbons other than methane. Methane and carbon monoxide are passed quantitatively to a GC column where they are separated. The methane is eluted first and passed unchanged through a catalytic reduction tube into the FID. Hydrocarbon concentrations, corrected for methane, are determined by subtracting the methane value from the THC value. The carbon monoxide measurement, which is obtained simultaneously in this method, is not required for the measurement of hydrocarbon corrected for methane and will therefore not be considered.

The range and sensitivity of the various commercial instruments will vary; however, the general range is 0 to 20 ppm of carbon as methane, and the methane detection range is 0 to 10 ppm (Katz, 1977).

GC Integrated with FID

Eaton et al. (1973) described a THC analyzer which combines GC and FID and is capable of monitoring THC as well as certain individual compounds in the atmospheric samples. The analyzer uses compressed air as the carrier gas and a hydrogen FID sensor and employs backflush chromatography to obtain the THC concentration. The backflushing allows two occurrences: first, the removal of methane and other compounds which interfere with the accuracy of the THC analysis; second, the grouping of remaining organic compounds to form a single measurable peak. The limit of detection is 1.0 mg/m^3. The analyzer is commercially available and has proven useful for air pollution analysis.

Burgett and Green (1976) described a system that automatically determines THC, carbon monoxide, and methane through only one injection per sample. The instrument used for this analysis is the Hewlett-Packard Model 5830A with dual FID. The analyzer consists of two modules, the chromatograph and a keyboard terminal. The column backflush technique used by Eaton is also employed for the determination of THC in this system. The detection limit of this system is 0.1 ppm. This type of system has wide application for other

air pollutants in addition to carbon monoxide, methane, and THC. For example, by changing the column, vinyl chloride may be analyzed at the parts per billion level.

Sentek (1969) described a sensitive and accurate FID analyzer for gases and vapors of organic compounds occurring in the workplace air. Upon ionization of the material, the intensity of the resultant ionization current is registered on a recorder and is proportional to the concentration of the substance to be determined. The analyzer can be used to detect specific organic compounds, gases, and vapors occurring in the workplace air or for determining the THC concentration. The analyzer is portable and can be fully automated.

Other Methods for Organic Gas Analysis

Gas chromatography/mass spectrometry (GC/MS) is used primarily for specific compound identification, and there are a number of reports in the literature on the use of GC/MS for the determination of individual organic vapors. These methods will not be considered in detail in this survey.

However, two recent reports which are representative of the use of GC/MS for air analysis of organic vapors are described briefly. Pellizzari et al. (1976) described the use of the Varian Mat CH 7 GC/MS 6201 computer and SCOT capillary column to identify over 100 aliphatic hydrocarbons in ambient air sampled in the Los Angeles Basin. No limit of detection was reported.

Evans and Arnold (1975) described the use of a portable MS for the detection of organic vapors and gases in ambient and workplace air. The system was developed by the U.S. Army and uses the UIT Model 100B quadrupole analyzer developed by Varian Associates which is capable of detecting organic vapors in the nanogram and picogram range. In this system, air is drawn across the face of a dual section silicone membrane separator. Since the dimethyl silicone membrane material is more permeable to organic molecules than to the air gases, the relative concentration of the sample is increased at each stage of the separator. The portable system has met requirements in industrial hygiene and organic environment monitoring.

Brady (1975) described the use of a Perkin-Elmer Model 900 GC equipped with a stainless steel capillary column and vapor phase IR spectrometry for the direct determination of complex organic vapors. This method can be applied to the analysis of any compound or mixture that can be chromatographed and give IR spectra. This is the first report in which a capillary column is coupled to a vapor cell for measurement of the IR spectrum of GC effluents. Brady applied this system to the analysis of coal tar distillates in which quantitative information was obtained from the chromatogram and identification of each compound was made from its IR spectrum. Hydrocarbons were found to have weak absorption, and 50 nl of each compound is typically required for reliable results. The lower limit of detection ranges from 5 to 50 nl depending upon the specific compounds to be analyzed.

The Byron Instruments, Inc., Model 233 is a fully automatic THC analyzer which combines GC with hydrogen FID to isolate and measure THC at the parts per billion level. This analyzer's principal use is ambient air measurements, but it can be used for source monitoring by changing the range. Carbon monoxide and methane are isolated from each other along with potential interferences such as moisture, nitrogen, and other air constituents by a special stripping technique and by molecular sieve separation columns. Carbon monoxide is converted to methane and measured by FID. This model is fully automatic.

The Byron Model 401 hydrocarbon analyzer employs GC to separate methane and nonmethane hydrocarbons and measures the level with a hydrogen FID. Nonmethane hydrocarbons from samples of ambient air and source locations are measured at levels as low as 0.24 ppb, since a mole of hydrocarbon containing n carbons will produce n moles of methane. Methane in the sample is measured at levels as low as 2 ppm.

WATER ANALYSIS

Several instrumental procedures for VOC analysis of water have been reported and reviewed by Kübler (1977) and Bortlisz (1976). All current methods are based on the complete oxidation of organics and determination of the carbon dioxide formed. The oxidation can be achieved by wet chemical decomposition or by direct combustion at high temperatures. Some of the instruments which are representative of the current analytical methods for VOC in water are listed in Table 2.

Wet Chemical Oxidation

For wet chemical oxidation, three methods are commonly used:

1. A hot mixture of concentrated dichromate, sulfuric, iodic, and phosphoric acid (Abrahamczik et al., 1970; Kübler, 1977).

2. Peroxydisulfate in dilute sulfuric or nitric acid with added silver nitrate (Ehrenberger et al., 1975; Baldwin and McAtee, 1975; Kübler, 1977).

3. Passage of oxygen through acidified solutions with the simultaneous irradiation by UV light (Goulden and Brookbank, 1975).

Some of the advantages of wet chemical oxidation methods are that large samples can be analyzed, low concentrations can be determined, and acid and salts do not interfere. Some disadvantages of these methods are that not all organic substances will oxidize quantitatively, so that additional oxidation is frequently required to completely oxidize volatile substances. In addition, the methods require a relatively long time for final determination, carbon can be introduced by reagents, and they are generally not suited for automation.

TABLE 2. INSTRUMENTS AND APPARATUS FOR THE DETERMINATION OF VOC

Instrument	Oxidation method	Combustion temperature	Method of determination of carbon dioxide	Method of TOC determination[a]	Determination of volatile organic carbon possible	Detection limit (mg C/liter)	Analysis time per sample	Reference
Beckman Model 915-A VOC analyzer	Combustion in air Cobalt oxide catalyst	950°C	Nondispersive IR analyzer	Difference	No	5.0	2 - 4 min	Van Hall and Stenger (1967)
				Purging	No	0.5	-	Kehoe (1976)
Ionics Labor VOC analyzer 445	Combustion in N_2 Oxidation catalyst	950°C	Nondispersive IR analyzer	Difference	No	0.5	3 - 4 min	Kübler (1971)
W. C. Heraeus VOC analyzer	Combustion in O_2 Copper oxide catalyst	900°C	Nonaqueous titration	Difference	Yes	0.2	8 min	Merz (1976)
H. Maihak VOC-UNOR	Combustion in air Oxidation catalyst	850°C	Nondispersive IR analyzer	Purging	Yes	0.1	20 min	Axt (1970)
Carlo Erba Model 420 total carbon monitor	Combustion in N_2 Copper oxide catalyst	950°C	Conversion to methane, integration of FID signal	Purging	Yes	< 1.0	5 min	Kübler (1977) Dol
Dohrman DC 52 VOC analyzer	Pyrolysis in He Cobalt oxide catalyst and/or UV light	850°C	Conversion to methane, integration of FID signal	Purging (at 110°C)	Yes	< 1.0	5 min	Takahashi (1972)
				Purging	Yes	1.0	5 min	Takahashi (1976)
Wösthoff Hydromat-VOC	Wet oxidation Dichromate/sulfuric acid	160°C	Conductivity measurement of absorbing solution	Purging	No	1.0	20 min 6 samples per hour	Schierjott et al. (1972) Ehrenberger (1973)
H. Maihak UV-DOC-UNOR	Wet oxidation with O_2 Irradiation with UV light	40°C	Nondispersive IR analyzer	Purging	Yes	0.01	3 - 12 min	Wolfel and Sontheimer (1974)
Technicon Instruments	Wet oxidation by sulfuric acid and potassium persulfate		Spectrophotometric measurement of titrated solution with CO_2	Purging	Yes	0.2		Jirka and Carter (1977)
Research by E. I. du Pont de Nemours and Company	Wet oxidation by inorganic acid		Conversion to methane, integration of FID signal	Difference	Yes		10 min	E. I. du Pont de Nemours and Company (1976)
Research apparatus by Fiedler et al. (1975)	Wet oxidation by inorganic acid		Air-gas electrode gas-permeable membrane	Difference	No	~ 10		Fiedlleret al. (1975)
Research instrument by Dobbs and co-workers	Combustion in O_2 Copper oxide catalyst	900°C	Reduction to methane, integration of FID signal	Purging	Yes	< 1.0		Dobbs (1967)

a/ The two methods used for TOC determination are (a) the difference method and (b) oxidation after removal of inorganic carbon by purging acidified samples.

Direct Thermal Combustion

Most of the VOC analyzers available today are based on oxidation of the sample to CO_2 in a combustion furnace at temperatures up to 950°C in a stream of oxygen with a catalyst present. The carbon dioxide from the decomposed sample is a measure of VOC. The method achieves complete combustion in a short time and is suited for automation. A disadvantage of the method is that, in some analyzers, the activity of the catalysts slowly decreases and the combustion tube is destroyed by water with high salt content (Kübler, 1977).

Determination of Carbon Dioxide

The methods used for the determination of VOC from the carbon dioxide formed by oxidation of carbon-containing materials are based on the following procedures:

1. Titration in a nonaqueous solvent (Metz, 1969) and measurement of electrical conductivity of alkaline absorption solution.

2. IR absorption with a nondispersive IR analyzer.

3. Reduction of carbon dioxide to methane and integration of the FID signal (Dobbs et al., 1967).

4. Retention of carbon dioxide on a molecular sieve column and integration of the thermal conductivity detector (Ehrenberger, 1973).

5. The measurement of CO_2 concentrations on a CO_2 specific electrode (Ruzicka et al., 1975).

The IR method is the most frequently used for VOC determinations. It is based on the measure of IR absorption of carbon dioxide with a nondispersive IR gas detector sensitive to CO_2.

The Beckman Model 865 IR analyzer based on the nondispersive principle has a sensitivity and reproducibility sufficient to detect 0.1 mg carbon per liter of water in a 2-µl sample (Kübler, 1977).

Instrumental Methods

The VOC analyzer developed by Axt (1970) is suited for carbon determination of surface and drinking water with low carbon content. Because of continuous sample supply and recirculation of the carrier gas, the working limit of detection is as low as 0.1 mg/liter. The analyzer is based on the formation of CO_2 by oxidation in a combution furnace and determination of CO_2 with an IR analyzer. This analyzer was developed for the VOC determinations of industrial wastewaters with high levels of VOC. The volatile organic substances are not lost in the removal of inorganic carbon but are returned to the combustion chamber as organic carbon, thus eliminating a separate determination by the difference method.

Takahashi (1976) describes a method using the Dohrmann DC52 VOC analyzer which also provides accurate determinations for low levels of volatile organic carbon and VOC in portable water samples. The method involves two procedures: (a) removal of volatile organic carbon compounds from the sample by sparging with an inert gas stream, followed by direct reduction pyrolysis to methane after carbon dioxide from inorganic carbonates is removed; and (b) the residual organics are oxidized to carbon dioxide with UV irradiation in the presence of an oxidizing agent (potassium persulfate and phosphoric acid in water), and the carbon dioxide is converted to methane. The methane produced in each of these steps is measured with an FID. Complete analysis time is less than 10 min per sample. The minimum detectable levels for volatile organic carbon and VOC are 1.0 and 10 µg/liter, respectively. Response to carbon is linear from 1.0 to 10,000 µg/liter, and reproducibility is within ± 2% or ± 5 µg/liter.

The same instrument can be applied to the determination of organic carbon in surface and seawater, as well as industrial wastewaters with high and low carbon contents (Kübler, 1977).

The Carlo Erba Model 420 is designed for fully automatic monitoring of VOC in water and water treatment plants and is suitable for analysis of discrete samples. It is based on the following principle. The sample is acidified, sparged free of inorganic carbon, and transferred by carrier gas to an oxidation chamber, and the resulting carbon dioxide is converted to methane by hydrogenation in the presence of a nickel catalyst. The methane, which is proportional to the concentration of dissolved organic carbon, is detected by an FID.

Carbon dioxide and volatile organic gases contained in the carrier gas are separated by a gas-liquid separator. The amount of volatile organic and inorganic carbon can be determined. The analyzer can be equipped with a data handling module which records and prints out directly the VOC, total carbon, and inorganic carbon values (Kübler, 1977).

Wölfel and Sontheimer (1974) developed an organic carbon analyzer based on the oxidation of aqueous solutions by oxygen under the influence of UV light; the carbon dioxide formed is measured by a nondispersive IR analyzer. The detection limit is as low as 0.1 mg carbon per liter; the sample size may range from 50 to 20,000 µl. The major component of the analyzer is the oxidation vessel, a cylindrical 300-ml Pyrex vessel into which a quartz mercury lamp is inserted. The vessel is maintained at 40°C and contains 300 ml of carbon-free water acidified with phosphoric acid to pH 2. A sample is introduced into the solution, and the dissolved organic substances are oxidized by oxygen bubbled through the solution in the presence of UV radiation from the mercury vapor lamp. The gas leaving the vessel is passed through a furnace at 600°C where volatile organic substances are also oxidized. The carbon dioxide concentration in the oxygen carrier gas is measured by a nondispersive IR analyzer.

The characteristics of this method are suitable for analysis of surface water and water from general sources. The disadvantages are that undissolved

organic carbon cannot be determined and some substances are difficult to oxidize, which would extend the time required for oxidation. The interferences caused by chloride ions can be eliminated by a sufficient amount of mercury II sulfate.

Thomas Kehoe of Beckman Instruments, Inc., described a catalytic combustion IR analysis technique that can be used for low level determination of VOC in the environment, such as effluents from sewage treatment plants, drinking water supplies, oil contamination in condensate, and various applications involving organics in production quality assurance. Concentrations of VOC as low as 1 ppm can be determined with this system. The method consists of the injection of a known volume of liquid sample into a ceramic tube maintained at 950°C and containing a catalyst of cobalt oxide. The vaporized organics are completely converted to carbon dioxide and swept by the carrier gas into a nondispersive IR analyzer. The IR analyzer provides total carbon analysis, which often contains inorganic carbon that must be removed by acidification and sparging or be measured and subtracted from the total carbon concentration. The inorganic carbon can be determined on a separate channel of the same instrument. The inorganic channel of the Beckman 915-A VOC analyzer, for example, consists of a glass tube containing quartz chips wetted with 80% phosphoric acid and maintained at 150°C. The carbon dioxide from the oxidized inorganic carbon is also swept by carrier gas to the IR analyzer. This inorganic carbon value is then subtracted from the total carbon to establish the true VOC concentration (Kehoe, 1976).

Schierjott and co-workers developed a method for VOC analysis which employs wet chemical oxidation of the organic constituents using a mixture of dichromate and sulfuric acid. Consequently, the method is not affected by high salt or acid contents and is particularly suited for the analysis of industrial wastewaters. The analyzer, manufactured by Wösthoff, is equipped for continuous monitoring of waste streams. The sample is sparged to remove carbon dioxide liberated by the dichromate-sulfuric acid mixture. The carbon dioxide formed is flushed via carrier gas into a conductivity cell where the CO_2 in the gas is absorbed in sodium hydroxide solution. The conductivity due to the absorption of carbon dioxide is a direct measure of the VOC content of the sample. Chlorine interferes in the sample and is removed by a chlorine absorber from the oxidation before measurements. The detection range is from less than 1.0 to 500 mg/liter (Schierjott et al., 1972; Kübler, 1977).

Merz (1976) has described a method for the determination of VOC in potable water, sewage, industrial effluent, and boiler feedwater. The carbon compounds in the sample are subjected to rapid catalytic combustion in a stream of oxygen at about 1000°C. The resulting carbon dioxide is titrated continuously and automatically with tetrabutyl ammonium hydroxide to give the value of total carbon in the sample. For the determination of total inorganic carbon, the sample is acidified and the evolved carbon dioxide is swept into an absorption cell for continuous titration. The difference between the total carbon and the total inorganic carbon yields the value of VOC. The advantages of the method over IR and conductivity detectors are that no volatile carbon compounds are lost, larger samples can be taken, and the colorimetric titration is linear over the entire range. The time required

for analysis is 8 min per determination, and sampling can be done manually or automatically. The apparatus is made by W. C. Heraeus, Germany, and distributed in the United States by Mettler Instrument Company.

The Technicon Instrument Corporation has developed a method for the determination of dissolved organic carbon (DOC). The VOC of a water sample is the sum of suspended organic carbon and DOC. In many ecological studies, a DOC test provides more information than VOC alone for predicting trends in water quality.

In this method, water samples are automatically sampled, acidified, and sparged with nitrogen to remove inorganic carbon. The organic carbon remaining in the sample is then converted to carbon dioxide using sulfuric acid and potassium persulfate solutions and UV light. The carbon dioxide then passes through a gas permeable dialyzer membrane into a buffered solution of phenolphthalein solution. The decrease in the phenolphthalein solution is proportional to the carbon dioxide concentration. The intensity is measured spectrometrically at 550 to 560 nm. The range for DOC is 0.2 to 20.0 mg carbon per liter. The detection limit is 0.2 mg carbon per liter or 2 ppm (Jirka and Carter, 1977).

The conventional method of measuring TOC in industrial wastewater using FID comprises acidifying the water sample with inorganic acid, sparging the acidified water sample with carbon dioxide-free air to remove carbon dioxide from the sample, oxidizing the organic carbon present in the sparged water sample to carbon dioxide, reducing the carbon dioxide to methane, and measuring the quantity of the resultant methane by flame ionization. The loss of volatile organics during the sparging can be avoided by a modified process whereby the air used to sparge the acidified water sample is collected and combined with methane obtained from the reduction step and then passed to an FID (E. I. du Pont de Nemours, 1976). Dobbs et al. (1967) also used a combustion reduction system to measure organic carbon in water by the hydrogen FID.

Fiedler et al. (1975) developed an air gap electrode for the analysis of VOC in wastewater and lake water. The VOC content is determined directly after wet chemical oxidation of the sample or after acidification with an alkaline potassium sulfate solution. The analysis can be done quickly and reliably with less than 3% deviation. The carbon dioxide measurements are made with gas sensing electrodes. The measured VOC content of water samples ranges from 13 to 170 mg carbon per liter. No detection limits were given.

SECTION 4

SELECTION OF ANALYZERS

The names of three organizations which are potential suppliers of VOC analyzers were obtained from the project officer. Contact was made with these three organizations. Additional potential suppliers of VOC analyzers, identified by the literature search, were also contacted.

EPA already owns a Byron Model 401 analyzer and is currently evaluating its performance.

Contact with Baseline Industries indicated that, from their component parts, a system which would perform total gaseous nonmethane organic carbon (TGNMOC) analysis could be obtained for a total cost of $5,375.

Dohrmann Division of Envirotech Corporation proposed supplying a system consisting of a Model DC-50 total organic carbon analyzer less the manual boat inlet. The pyrolysis tube would be modified to minimize peak spreading and to mate with a heated sampling valve. The catalyst would be modified to withstand sulfur and the bypass column modified to separate CO, CO_2, and CH_4. The quoted price was $9,000.

Analyzers made by Baseline, Byron, and Dohrmann were the only instruments that were located. All other contacts were negative. Beckman, MSA, and Horiba could supply components which could be assembled into a potential analyzer but could not supply a total system.

Since EPA was already evaluating the Byron instrument, it was decided that the Baseline and Dohrmann instruments would be evaluated in this program. A Baseline TGNMOC analyzer and a Dohrmann modified Model DC-50 were therefore obtained for evaluation.

SECTION 5

LABORATORY EVALUATION

The two analyzers were initially set up in the laboratory to verify that they were working properly. Each analyzer was then to be tested on three different simulated process streams. These processes are for ethylene oxidation, maleic anhydride/benzene oxidation, and acetone/phenolcumene production.

BASELINE ANALYZER

The Baseline instrument does not appear to be capable of functioning satisfactorily due to a problem in the oxidizer. Some modifications were made in an effort to overcome the Baseline limitations without success.

The instrument was operated in a laboratory environment where it produced random activations of the sampling valves. This problem was traced to an apparent overheating of the microprocessor. Operating with the cover removed eliminated the overheating and resultant random valve activation.

The second problem related to the way the system was set up. The original flow diagram is shown in Figure 1. With this flow system, methane and CO_2 were separated from the other hydrocarbons and fed to the FID. The remainder of the hydrocarbons were then backflushed from the column and fed to the FID. It was found that when analyzing the required gas samples containing 1 to 5% CO_2 (10,000 to 50,000 ppm), the CO_2 tailed and interfered with the THC analysis. The system was replumbed as shown in Figure 2. Operating with a mixture of CH_4, CO_2, CH_2H_4, and C_2H_6, the valves were programmed to reject (dump) CH_4 and CO_2 and switch to the backflush mode just prior to the appearance of the ethylene. Ethylene was the third component to be eluted.

A typical program for the modified Baseline analyzer would be:

0 sec - Sample valve in fill position (solid lines)
Vent valve in detector position (solid lines)

1 sec - Vent valve to vent position (dotted lines)

The column is still in backflush mode

2 sec - Sample valve to sample position (dotted lines)

The column is now in forward flush mode. Methane, carbon monoxide, and carbon dioxide are vented.

75 sec - Vent valve to detector position (solid lines)

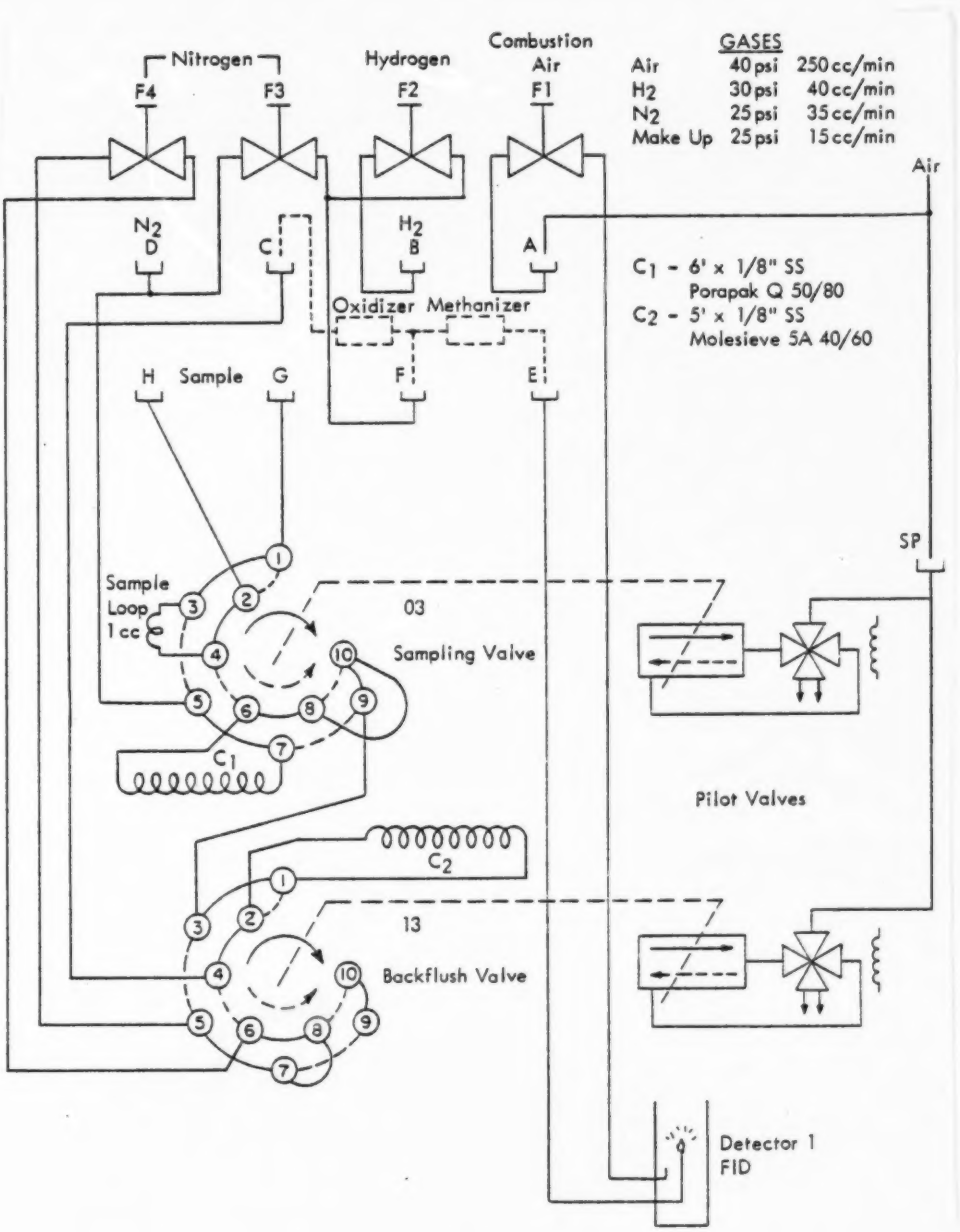

Figure 1. Original Baseline system.

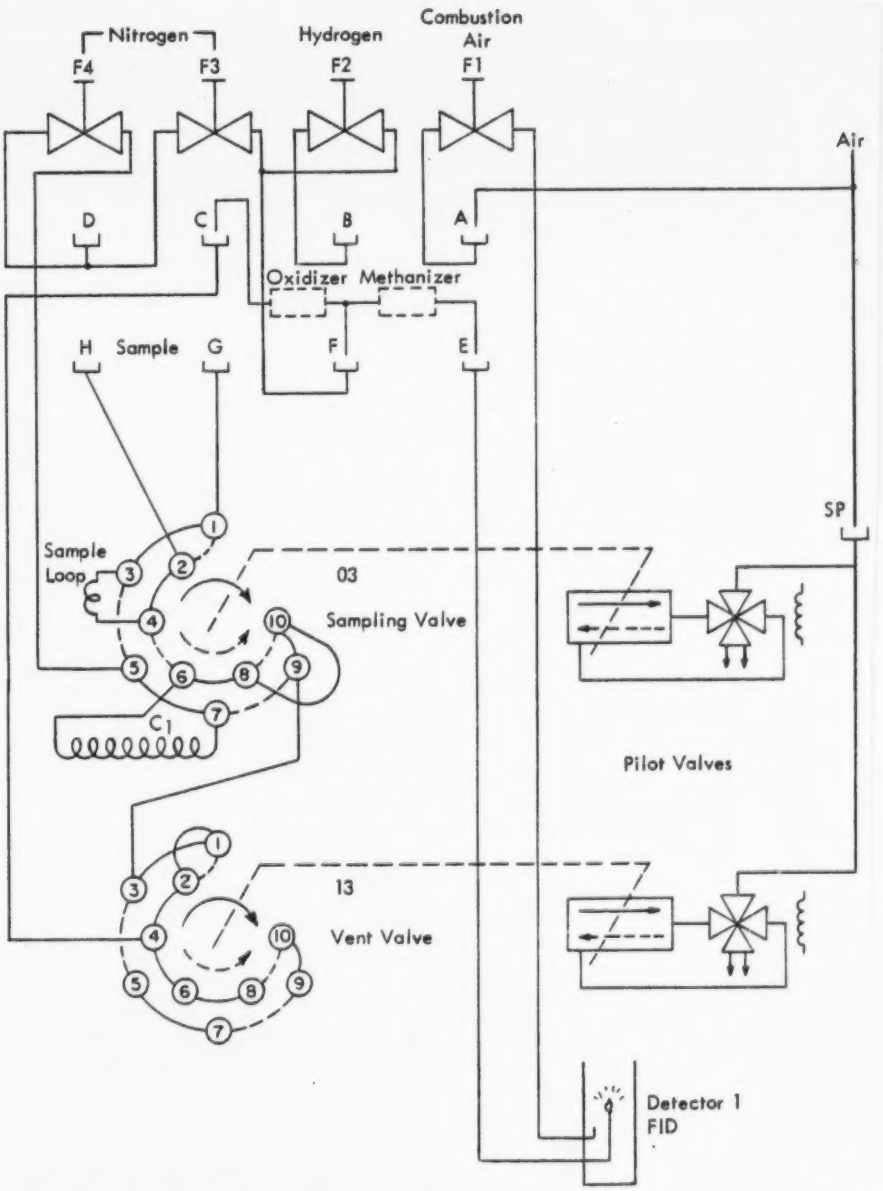

Figure 2. Modified Baseline system.

VOC are now sent to the oxidizer-reducer and the detector. In normal use, the sample valve is also returned to the fill (backflush) position at this time. During the lab tests to measure resolution of the light components, no backflush was performed.

Figure 3 shows some typical results using the modified flow system. The section of the chromatogram labeled A shows the analytical results from a mixture of 1,000 ppm of C_2H_6, 4,000 ppm of ethylene, 50,000 ppm (5%) carbon dioxide, and 500 ppm of methane. The oxidizer was off and the methanizer was on. All of the CH_4 and most of the CO_2 was being rejected. The C_2H_4 (first peak) and C_2H_6 (second peak) were recovered quantitatively. The two hydrocarbons are superimposed on the long low peak from residual CO_2 in the system from tailing. The section labeled B is not an actual chromatogram but is presented to show the resolution obtained between methane and ethylene. The CO_2 maxima lies in between the CH_4 and C_2H_4 peak. The section labeled C shows a CO_2, C_2H_4, and C_2H_6 mixture with the methanizer and oxidizer off. Repeat runs under the same conditions gave results that were reproducible within 5%.

Figure 4 shows the problem found with the oxidizer operation. Section A shows the results from a mixture of CH_4, CO_2, C_2H_4, and C_2H_6 without operation of the dump mode and with the oxidizer and methanizer off. Section B shows the results with the dump valve operating a maximum CH_4 and CO_2 rejection and the methanizer and oxidizer off. Section C shows the same mixture with maximum CH_4 and CO_2 rejection and the methanizer on and the oxidizer off. The degree of baseline shift caused by the residual CO_2 from tailing can be seen by comparing B and C. Section D shows the results of operating in the same mode as C with the exception that the oxidizer is now on. The hydrocarbons have apparently been oxidized (or destroyed). The methanizer should convert the oxidized products (CO_2) to methane, but it does not appear to be capable of reducing the oxidized products. It is known that the methanizer is working because the system responds to CO_2. This would not be the case if the CO_2 were not being reduced to CH_4. All operating parameters of the oxidizer were investigated without recovering a response to C_2H_4 and C_2H_6. Once the oxidizer becomes hot enough to function (535°C minimum), a response can no longer be obtained. Due to the limited time available on the contract for trouble shooting, the Baseline instrument evaluation was halted at this point.

DOHRMANN ANALYZER

The Dohrmann DC-50 is normally used for analysis of carbon in water. Figure 5 is a block diagram of the analyzer in the vent mode. Figure 6 shows the analyzer in the organic backflush mode. Several modifications were necessary to adapt this unit for volatile nonmethane gaseous sample analysis. The boat inlet was replaced by a heated Carle 8-port sampling valve with 10-cc sample loops. A modified bypass column was installed by Dohrmann consisting of a 30 cm length of 50% Chromosorb 101 and 50% Chromosorb 102 packing.

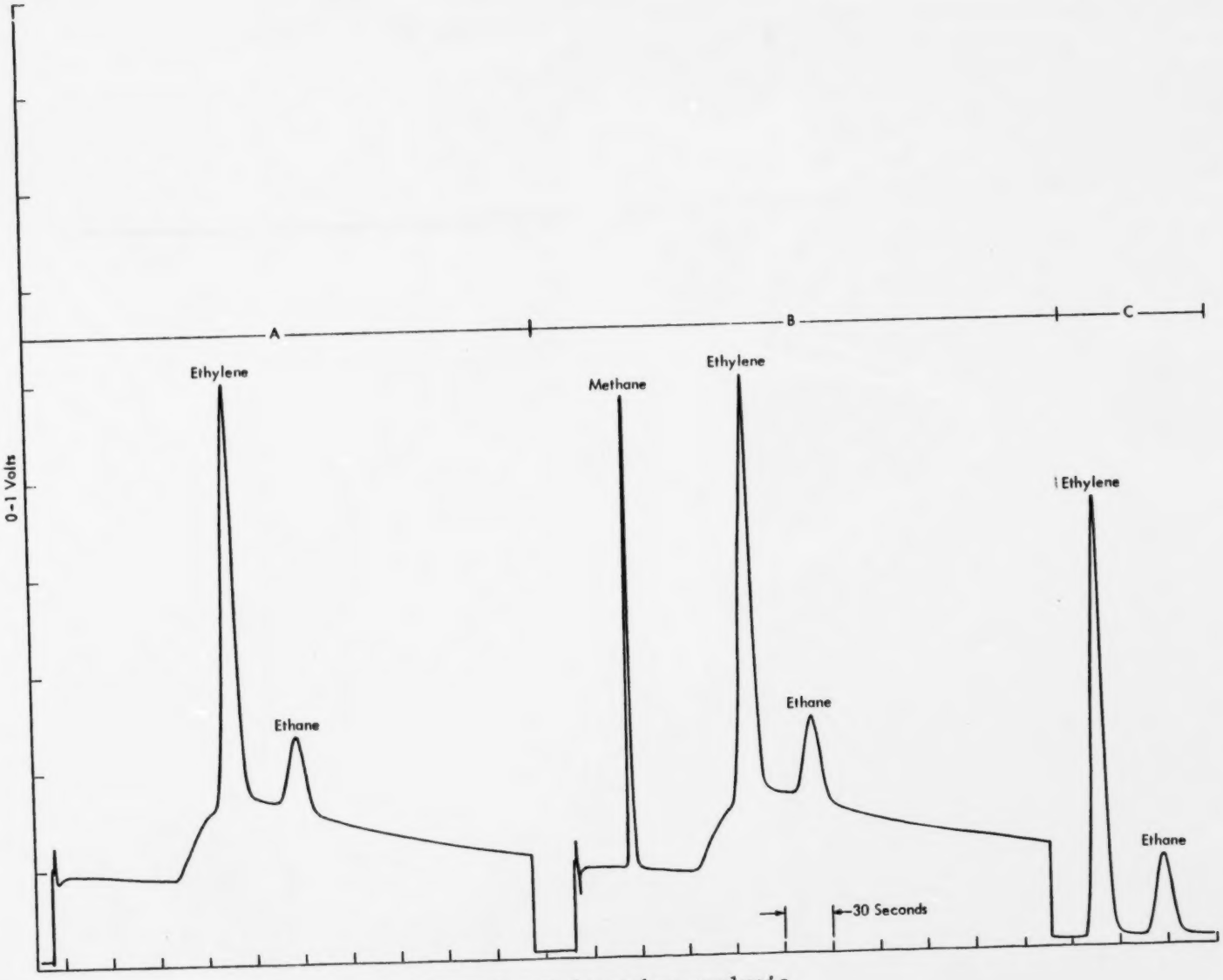

Figure 3. Hydrocarbon analysis.

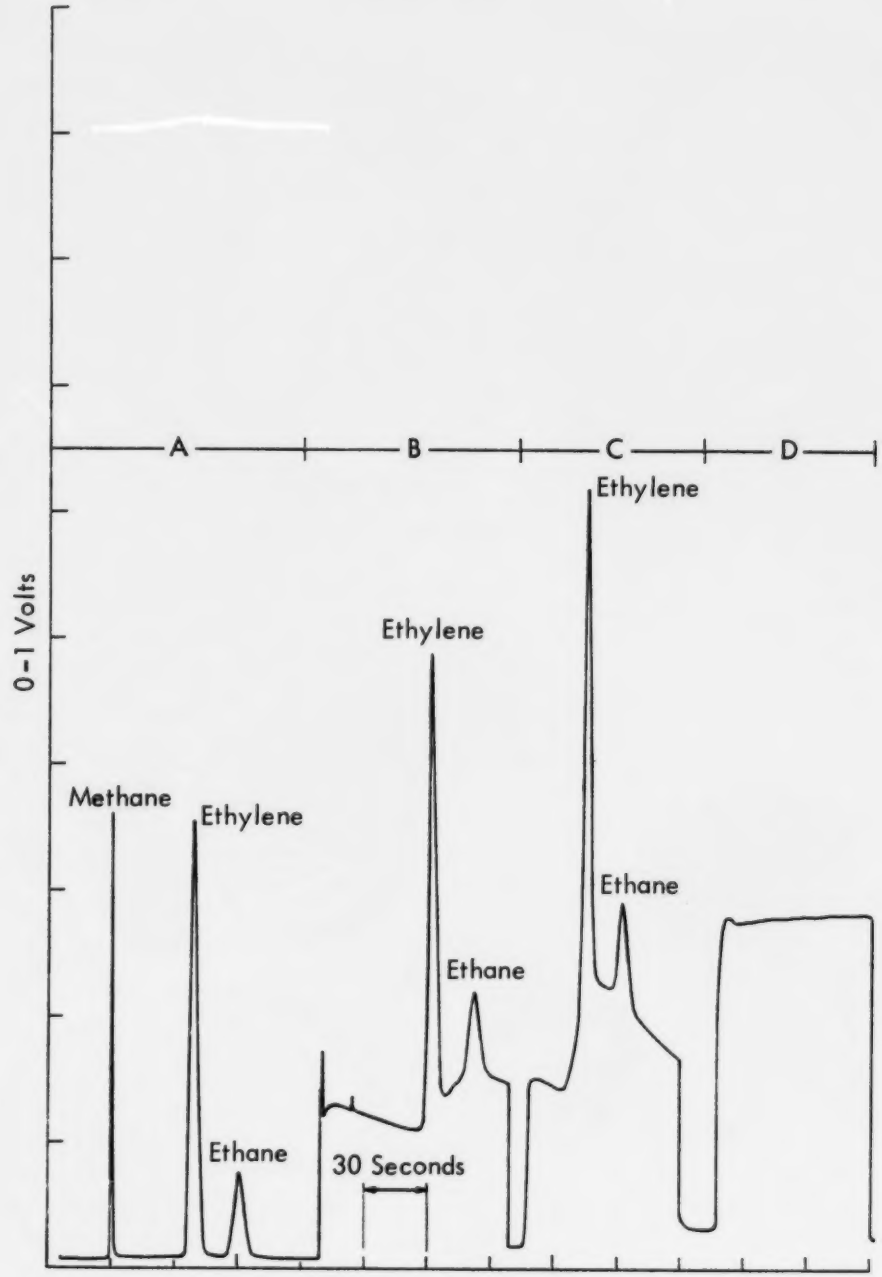

Figure 4. Oxidizer operation.

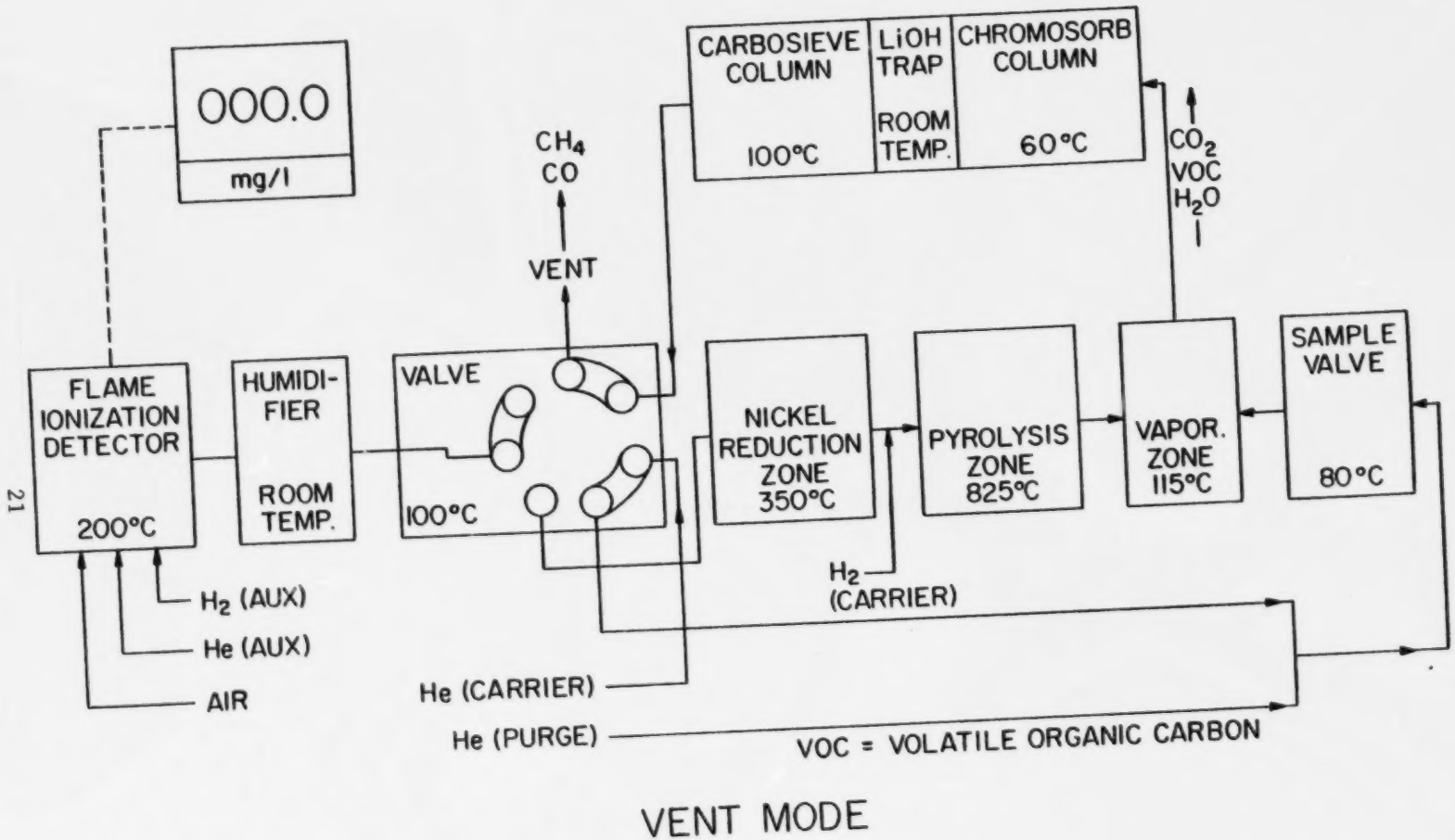

Figure 5. DC-50A/52A OC-direct mode, vaporization step, CO_2 venting.

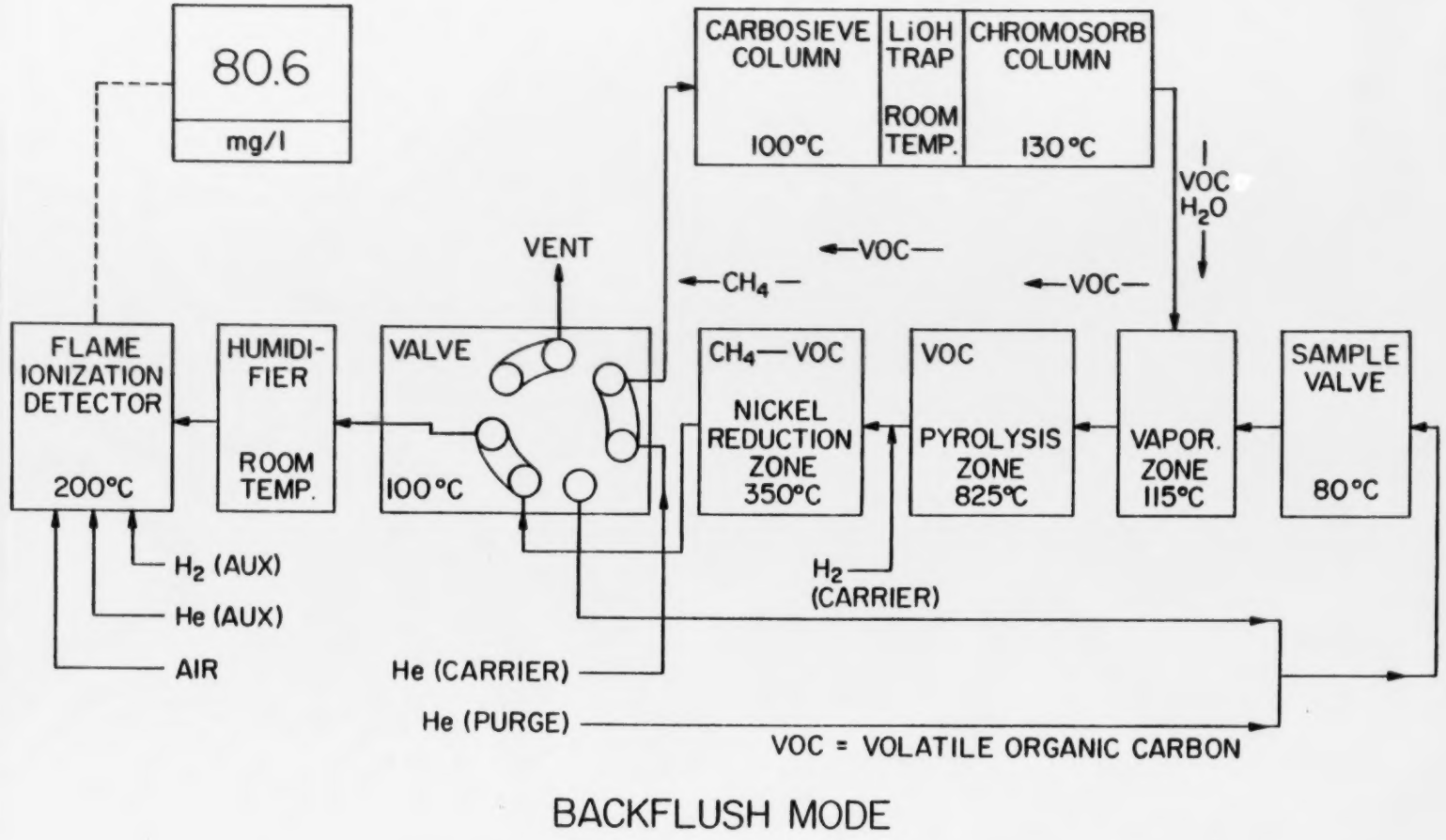

Figure 6. DC-50A/52A, OC-direct mode, vaporization step, backflushing.

This column gave complete venting of methane and carbon monoxide, but CO_2 co-eluted with the C_2 hydrocarbons. A 25 cm x 1/4 in. O.D. stainless column packed with 60/80 mesh Carbosieve B was installed by Dohrmann in the valve oven. This column was attached in series with the bypass column and obtained retention of the C_2 hydrocarbons and separation of moderate amounts of CO_2 with the oven temperature at 120°C. Rather than lose some of the C_2 fraction to ensure complete CO_2 venting, a short glass U-tube packed with 8/12 mesh lithium hydroxide (~ 0.5 g) was mounted on the outer valve door and connected between the Carbosieve column and the valve by Dohrmann.

With these modifications, the system completely rejects methane, carbon monoxide, and CO_2 while retaining the C_2 hydrocarbons. The LiOH trap is theoretically capable of absorbing 400 to 500 injections of 5% CO_2. The usable capacity is the equivalent of 150 injections at 5%. Beyond this point, from 2 to 5% of the CO_2 present will be included in the VOC concentration.

SIMULATED PROCESS SAMPLE TESTS

After the initial tests of the Dohrmann analyzer indicated that it was functioning properly, it was subjected to a series of tests using three different simulated process stream mixtures. The nominal compositions for the mixtures are:

1. Oxidation of ethylene process

Ethane 500-1,000	Ethylene oxide 100
Ethylene 3,000-4,000	Oxygen 5-50%
Carbon dioxide 5%	Water 10%

2. Maleic anhydride - benzene oxidation
   - Benzene 500
   - Hexane 100
   - Acetaldehyde 50
   - Carbon dioxide 3%
   - Oxygen 12%

3. Acetone/phenol - cumene process
   - Cumene 1,000
   - Acetone 200
   - Benzene 300
   - Methanol 300
   - Oxygen 30-80%
   - Carbon dioxide 1%

In all cases, balance gas is dry nitrogen. At least one of the hydrocarbons in each mixture must be variable over a 2:1 range.

The calibration system uses a combination of pressurized cylinder gas mixtures, permeation tubes, and syringe pump injection to generate the mixtures. A pair of calibrated rotameters were used to meter the flow of the low pressure cylinder gases prepared by Scott Specialty Gases. The combined flow from the rotameters then passed through a large water-jacketed permeation

tube holder and then to an injection tee and a Sage Model 355 variable speed syringe pump. The injection tee and all downstream lines were heat traced to obtain efficient vaporization in the injector and to maintain the water content of the ethylene mixture of the desired 10%.

The ethylene mixture used a mixture of ethane, ethylene, and CO_2 in nitrogen in one rotameter, air in the second rotameter, an ethylene oxide permeation tube, and water injected by the syringe pump.

The benzene/maleic anhydride process mixture used a hexane and CO_2 mixture in one rotameter, air in the second rotameter, acetaldehyde from a permeation tube, and benzene injected by syringe pump.

For the cumene mixture, an oxygen and CO_2 mixture was used in a single rotameter, and a cumene, acetone, benzene, and methanol mixture added by the syringe pump.

The only problem with the calibration system was leakage in the syringes or fittings with higher gas flow rates due to the back pressure in the sampling valves. The leakage was insignificant at gas flow rates < 100 cc/min and syringe pump rates to empty a syringe in less than 3 hr. Under these conditions, the injection rate remained constant within a few percent. Mixtures of propane in nitrogen were used for initial calibration.

Table 3 shows the results of the tests of the three simulated processes using the Dohrmann analyzer. A 2,010 ppm (6,030 ppm C) propane in nitrogen gas was used as the standard for all runs. Each series consisted of at least four injections at the test level. A similar number of injections were made for the standard and for the system blank each day. The blank reading was subtracted from all readings. Series 1 and 2 were made at abnormal water levels due to a miscalculation of injection rates. The results for 1 and 2 should be high, because water condensation occurred in the sample lines, thus raising the organic content above the calculated values. Series 3 was then run to verify that the primary error in the first two series was the water content. Series 12 through 16 were subject to breakthrough of the LiOH column after about 150 injections (with CO_2). This was verified by the results shown in Table 4. A further problem was that the calibration gas was flowing constantly through the sample valve, and at the higher flow rates the pressure in the sample loop was significantly above ambient. This flow rate effect is illustrated by the data in Table 5. Since the calibration gas was usually flowing at 20 cc/min, the increased flow rate of the test gases caused high results. The corrected percent theoretical line of Table 3 includes a correction for the pressure effect. The blank reading (obtained by cycling the system, but not throwing the sampling valve) during these tests was betweeen 100 to 200 ppm as C. It was stable after the initial warmup each day and slowly decreased during each succeeding day of use. Although the blank is subtracted from all readings, it appears that the high background tends to lead to high results at the lower organic levels (Series 1, 5, 8, 11). This tendency is clearly seen in the linearity tests reported in the next section. The results of Series 4 through 11 show a range of 89 to 115% for the corrected values and an overall average yield of 99.6% of the theoretical values.

TABLE 3. SUMMARY OF RESULTS - LABORATORY SIMULATION OF PROCESS STREAMS

	Ethylene process					Cumene process			Maleic anhydride process							
	1[a]	2[a]	3[a]	4	5	6	7	8	9	10	11	12[b]	13[b]	14[b]	15[b]	16[b]
CO_2%	2.3	3.3	5.0	4.4	2.9	1.0	1.0	1.0	9.3	13.9	9.3	3.7	3.5	3.4	9.4	9.4
O_2%	25.7	4.0	6.2	5.6	33.5	30.0	30.0	30.0	14.4	11.2	14.4	18.3	18.4	18.5	14.3	14.3
H_2O%	29.7	34.2	0	12.0	10.9											
Ethylene ppm	1,154	2,571	3,923	3,440	1,430											
Ethane ppm	280	799	1,218	1,070	348											
Ethylene oxide ppm	73	84	128	116	105				100	140	100	103	98	100		
Cumene ppm						990	876	359								
Benzene ppm						501	491	201	601	392	262	212	202	469	196	449
Acetone ppm						303	594	244								
Methanol ppm						440	216	89								
Hexane ppm									93	138	93	37	35	113	94	311
Acetaldehyde ppm															48	48
Total flow cc/min	140	100	78	70	45	94	96	96	135	101	135	97	102	100	105	105
Total C_1 ppm	3,014	6,908	10,538	9,250	3,765	12,960	12,230	5,010	4,360	3,460	2,330	1,700	1,620	3,690	1,840	4,660
Measured C_1 ppm	3,770	7,530	10,720	9,870	4,350	12,220	12,130	5,200	4,482	3,556	2,533	2,090	2,080	4,530	2,440	5,990
% theoretical	125.1	109.0	101.7	106.7	115.6	94.3	99.2	103.8	102.8	102.8	108.7	122.9	128.6	122.7	132.9	128.7
% theoretical corrected for pressure	118	103	99	104	115	89	94	99	96	98	102	118	124	118	128	124
				110%			94%			99%						

a/ Water content is outside normal range.
b/ Probable breakthrough of LiOH during these runs.

TABLE 4. EXHAUSTED VERSUS FRESH LiOH COLUMN RESULTS

Test gas = 30% CO_2, 988 hexane in nitrogen

Results following Series 16 = 7,113 ppm C, 120% of true value
Results with fresh LiOH = 6,049 ppm C, 102% of true value

TABLE 5. ERROR CAUSED BY FLOW RATE INDUCED BACKPRESSURE

Flow rate (cc/min)	Measured value (counts)	Error (versus zero flow)
0	3,654	-
20	3,680	+0.7%
66	3,762	+3.0%
96	3,855	+5.5%

During Series 9 through 14, the wrong tube was installed in the permeation chamber; however, acetaldehyde and ethylene oxide have very similar properties.

LINEARITY AND PRECISION

The instrument was tested with propane in nitrogen gases over the range of 10 to 10,000 ppm propane as shown in Table 6. The blank was 100 ppm C during this series which led to a large error in the low concentrations. The second test for linearity (and precision) was completed at the end of the program. The results of this test are shown in Table 7. The error of the 10 ppm propane gas was 9.1% versus the 99 ppm gas, a large improvement over the 108% error between these two gases in Table 6.

The low end linearity appears to be strongly dependent upon the blank level which can be improved only by constant use and care in maintaining pure carrier gas. Standard grade helium with a molecular sieve trap was used throughout this evaluation. The instrument manufacturer indicates that the blank should drop even further with steady use.

TABLE 6. LINEARITY CHECK-PROPANE, 10-10,000 PPM

Concentration	Net count	Measured conc.	Error
10.3 ppm	46	76 ppm C	+146%
98.9 ppm	213	354 ppm C	+19%
2,010 ppm	3,753	6,239 ppm C	+3.5%
9,770 ppm	17,630	reference	-

TABLE 7. PRECISION TEST AND FINAL LINEARITY CHECK

Mixture	ppm C	Average counts	σ(counts)	ppm C measured
10.3 ppm propane	30.9	266	8	33.7[a/]
99 ppm propane	297	1,330	18	reference
blank	0	130	4	32

a/ Net ppm C after subtracting blank.

SECTION 6

FIELD TEST

Following the successful completion of the laboratory evaluation of the Dohrmann analyzer, a field test of the unit was arranged. The field test plan included four runs per day for 4 days at a maleic anhydride plant.

It was originally intended that a second VOC analyzer would be field tested. However, the Baseline unit had failed the laboratory tests, and the EPA-owned Byron instruments were being rebuilt at the factory. The plant stream sampled was the process vent at a point between the two scrubbers. The gas was saturated with water at moderate positive pressure and slightly above ambient temperature. A midget impinger was used for water knockout, and each sample was collected over a 1-hr period in a 40-liter Tedlar bag.

The analyzer readings were compared with the results by GC/FID using the EPA method for benzene (Method 110). The GC used was a Varian Model 2440 using an FID, a 2 m x 1/8 in. O.D. stainless steel column packed with 5% SP-1200/1.75% Bentone 34 on 100/120 mesh Supercoport, and a heated gas sampling valve with matched 2 cm^3 sample loops. The column was operated at 100°C, and the sampling valve was at 70°C. The GC results were analyzed by a disk-based microcomputer system. Peak analysis used a moving 7-point average trigger function with compound peak measurements using a vertical extension to baseline at valley minima.

Both instruments were calibrated on the same mixtures. The primary calibration was with an 858 ppm benzene in nitrogen gas. Secondary calibration checks used a mixture of benzene (major component) with hexane and acetaldehyde in a 5% CO_2 stream with nitrogen balance and the same mixture with air dilution of about 4:1, air/mixture. An 858 ppm benzene air and a 988 hexane 30% CO_2 mixture were blended as needed from pressurized cylinders through calibrated rotameters. Acetaldehyde was added constantly from a permeation tube assembly. Since the permeation tube assembly did not have a bypass, acetaldehyde was present in all of the calibration gases. The calibration gas line was opened briefly before each injection to allow the valve contents to reach ambient pressure.

The digital panel meter on the Dohrmann analyzer failed during the set-up day but was replaced by a factory representative early on the first day of testing. No other problems occurred during the field test.

The results obtained with the Dohrmann analyzer are presented in Tables 8 and 9. The GC results and a summary comparison with the Dohrmann analyzer are shown in Table 10.

TABLE 8. DOHRMANN ANALYZER-FIELD TEST RESULTS

Sample No.[a]	Samples: Analyzer counts[b]			Calculated C_1 (ppm)		Calibration data: First blanks		Second blanks	First set of reference readings		Second set of reference readings	
1	7,046	7,107	7,210	2,833		225		197	12,633		13,205	
2	7,247	7,341	7,353	2,929		213		192	13,554		12,740	
3	7,422	7,081	7,272	2,901		212		194	13,139			
4	7,259	7,017	7,078	2,821	Median		203			13,055		
					Net				12,852	(5,273)[c]	2.437[d]	
5	6,194	6,337	6,405	2,870		142		104				
6	5,979	5,976	6,025	2,705		119		135	10,469		11,933	
7	4,728	4,801	4,796	2,159		123		116	11,198		11,813	
8	4,947	4,798	4,991	2,229		140		135	11,200			
					Median		128			11,535		
					Net				11,407	(5,270)[c]	2.165[d]	
9	6,196	6,313	6,166	2,385		136						
10	6,258	6,238	6,236	2,402		126		121	12,296		13,617	
11	6,032	6,178	5,965	2,321		158		136	13,633		13,331	
12	6,356	5,826	6,006	2,311		146		143	13,698			
					Median		138			13,554		
					Net				13,416	(5,264)[c]	2.549[d]	
13	5,773	5,848	5,632	2,249		153		87	13,454		13,582	
14	5,860	5,886	5,646	2,284		147		110	13,053		13,400	
15	5,728	5,762	5,909	2,245		143		106				
16	5,804	5,948	5,662	2,261								
					Median		126			13,372		
					Net				13,246	(5,276)[c]	2.511[d]	

Note: CO_2 content for all samples was 2.5-3.0%.

[a] A 1-hr integrated gas sample in a Tedlar bag.
[b] Underlined value is median-used in calculations - 858 ppm benzene plus acetaldehyde (Dean and Dixon, J. Anal. Chem., 23, 636-638, 1951).
[c] Total concentration C_1.
[d] Response factor - net counts/ppm C_1.

TABLE 9. FIELD TEST-SECONDARY CALIBRATION CHECKS

		Benzene/hexane						Benzene/hexane/air[c]					
		Benzene (ppm Cl)	Hexane (ppm Cl)	% CO_2	Total Cl[a]	Reading	Total found ppm Cl[b]	Benzene (ppm Cl)	Hexane (ppm Cl)	% CO_2	Total Cl[a]	Reading	Total found ppm Cl[b]
Run Nos. 1-4	Before	4,335	936	4.7	5,376	13,215	5,339	1,037	197	1.0	1,260	3,678	1,426
						13,419	5,423	1,390	172	0.9	1,596	3,723	1,444
						13,088	5,287						
	After	4,273	1,008	5.1	5,381	13,634	5,511	1,061	181	0.9	1,268	3,316	1,277
						13,090	5,288					3,532	1,366
												3,547	1,372
Run Nos. 5-8	Before	4,356	912	4.6	5,364	11,864	5,421	871	112	0.6	1,010	2,691	1,184
						11,651	5,322					2,553	1,120
												2,739	1,206
	After	4,508	737	3.7	5,358	11,783	5,383	1,379	221	1.1	1,634	3,702	1,651
						11,824	5,402	1,038	78	0.4	1,142	3,756	1,676
						11,912	5,443	1,024	212	1.1	1,262	3,194	1,416
								1,035	153	0.8	1,214	3,036	1,343
Run Nos. 9-12	Before	4,776	429	2.1	5,325	14,019	5,445	1,045	152	0.8	1,223	3,759	1,421
		4,623	605	3.1	5,330	14,380	5,587					3,852	1,457
												3,866	1,463
	After	4,570	666	3.4	5,348	13,821	5,368	1,043	167	0.8	1,236	3,345	1,258
						13,649	5,301					3,464	1,304
Run Nos. 13-16	Before	4,549	689	3.5	5,354	13,379	5,278	1,000	169	0.9	1,195	3,278	1,255
						13,440	5,302					3,171	1,213
	After	4,563	674	3.4	5,350	13,951	5,506	1,035	153	0.8	1,214	3,554	1,365
						13,534	5,340					3,451	1,324

a/ Total concentration Cl including acetaldehyde.
b/ Value obtained from response to the benzene reference (see Table 8).
c/ Accuracy of air rotameter limited to ± 10%.

TABLE 10. GC DATA SUMMARY AND VOC COMPARISON

Run No.	Retention time (sec) ppm as Benzene: C1-2 (57)	C4 (78)	Benzene (129)	C7-8 benzenoids (345)	C7-8 benzenoids (378)	C7-8 benzenoids (399)	C7-8 benzenoids (453)	GC total nonmethane hydrocarbons: ppm as Benzene	ppm C1	Dohrmann VOC: ppm C1	Difference
1	1.6/ -	- -	427/477	3.9/ -	2.6/4.1	5.7/6.7	2.3/2.1	468	2,806	2,833	+1.0%
2	1.8	2.5	448	1.3		1.5	1.2	454	2,727	2,929	+7.4%
3	1.5/2.0	- /0.2	477/449	2.3/1.9	1.6/1.4	3.5/2.7	1.5/1.2	471	2,827	2,907	+2.6%
4	1.3/1.3	1.0/ -	486/488	2.3/1.5	1.6/ -	3.8/0.5	1.6/0.4	497	2,981	2,821	-5.4%
5	1.4/1.3	0.8/0.9	480/452	2.0/2.0	1.3/1.3	3.0/3.1	1.1/ -	474	2,845	2,870	+0.9
6	1.2/1.3	1.3/ -	449/438	2.0/2.4	1.3/1.4	3.1/3.6	1.2/1.3	453	2,718	2,705	-0.5
7	1.1/1.2	0.22/1.3	340/344	2.0/2.0	1.3/1.4	3.0/2.9	1.1/1.1	350	2,102	2,159	+2.7
8	0.87/1.5	0.05/ -	373/362	2.1/2.1	1 4/1.5	3.2/3.2	1.2/1.2	375	2,253	2,229	-1.1
9	- /0.8	- /0.8	367/359	3.9/3.7	2.6/2.5	5.6/5.4	2.0/1.9	378	2,266	2,385	+5.3
10	1.0/0.9	0.7/0.9	378/354	3.3/3.4	2.1/2.0	4.9/4.8	1.7/1.7	379	2,272	2,402	+5.7
11	- /0.8	- /0.9	376/354	2.3/2.3	1.4/1.6	3.3/3.2	1.2/1.1	374	2,245	2,321	+3.4
12	0.8/0.8	- -	346/343	2.2/2.2	1.5/1.5	3.1/3.1	1.1/1.1	352	2,114	2,311	+9.3
13	1.0/1.3	- /1.0	329/348	2.1/ -	1.3/ -	3.3/ -	1.1/ -	347	2,084	2,249	+7.9
14	1.8/2.0	0.9/0.3	372/367	2.0/2.4	1.1/1.6	2.4/3.2	- /1.0	378	2,265	2,284	+0.8
15	1.2/1.1	1.4/0.3	323/357	2.3/2.4	1.5/1.3	3.3/3.4	- /0.9	349	2,093	2,245	+7.3
16	0.9/0.9	0.5/0.9	323/360	2.0/2.0	1.4 1.4	3.0/3.1	1.0/1.0	350	2,098	2,261	+7.8
								Average	2,418	2,494	3.1%
										σ = 96 (4.0%)	

A tendency for the Dohrmann results to be higher than the GC data during the last runs is not due to CO_2 breakthrough of the LiOH column, since the standards which contained CO_2 showed no increase in carbon content reading. The overall precision and comparability for the GC and Dohrmann indicate that the Dohrmann does perform satisfactorily under field conditions at maleic anhydride processes. Note that this test cannot demonstrate the accuracy of the results but rather the equivalence of the VOC method with the summation of all observed GC peaks. Since maleic anhydride process streams have benzene representing more than 90% of all organics, no corrections were made for the response factors of the nonbenzenoid peaks. The GC column used never allowed the elution of acetaldehyde during the calibrations. If it or similar compounds were present in the sample, they were not eluted from the GC column. Thus, the GC results may be slightly low.

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